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(54) Catalytic cracking of hydrocarbons

(57) A novel catalyst is produced by concentrating non-organic elements found in used lubricating oil. Chemically refining used lubricating oil with a strong acid yields a concentrated residue which produces a porous solid when remaining hydrocarbons are thermally cracked whilst passing a hydrocarbon gas through the residue. In the porous solid, the non-organic elements from the used lubricating oil are embedded in a carbon-based matrix.

The catalyst may be used to crack long-chain hydrocarbons at temperatures as low as about 320°C in the presence of hydrogen or a hydrocarbon gas.

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Description

[0001] The present invention relates to catalytic cracking of hydrocarbons, and particularly but not exclusively to a novel catalyst, a method of producing the same, and a method of catalytically cracking hydrocarbons.

[0002] Conventionally, long chain hydrocarbons (e.g. vacuum bottom product, and fuel oil containing heavy hydrocarbons to lighter cuts) may be broken down into shorter chain hydrocarbons (e.g. gasoline, kerosene, gas oil and light lubricating oils) either by thermal cracking or by catalytic cracking in the presence of hydrogen gas. In the latter process, temperatures are typically in the region of 480-510°C, although higher temperatures may be achievable with zeolite catalysts.

[0003] The present applicant has invented a new catalyst for cracking heavy hydrocarbon chains and reforming them into useful products and cuts. The new catalyst may be used in a novel process for cracking the long-chain hydrocarbons and producing more useful shorter chain hydrocarbons.

[0004] In accordance with a first aspect of the present invention, there is provided a method of producing a catalyst for cracking hydrocarbons, comprising: providing a used lubricating oil comprising traces of non-organic elements; and concentrating the non-organic elements.

[0005] The used lubricating oil may be petroleum based or synthetic in origin. Lubricating oils from petroleum consist essentially of complex mixtures of hydrocarbon molecules, although trace quantities of certain metals may be present if carried over from the crude oil precursor. Typically, the lubricating oil will contain pre-selected additives (such as oxidation inhibitors, anti-wear agents and detergents/dispersants), chosen to suit particular uses, e.g. automotive, hydraulic, aircraft. However, during use, the lubricating oil will acquire a whole range of additional components (non-organic elements) through contact with surfaces being lubricated.

[0006] The used lubricating oil may comprise at least a plurality of non-organic elements selected from the group consisting of: magnesium, aluminium, silicon, phosphorus, sulphur, chlorine, potassium, calcium, titanium, iron, copper, zinc, molybdenum, tin and lead.

[0007] The non-organic elements may be concentrated by chemically refining the used lubricating oil to produce an acidic residue, and cracking hydrocarbons in the acidic residue. The used lubricating oil may be chemically refined using a strong acid, for example sulphuric acid. Residual acid helps to provide an acidic environment which is beneficial to the cracking process ultimately used.

[0008] A batch of used lubricating oil may be concentrated by a factor of 4 in this way. In other words the acid residue yield may represent about 20-25% by weight of the batch of used lubricating oil at the start. However, the vast majority of non-organic elements in the used lubricating oil are present in the acidic residue.

[0009] Hydrocarbons in the acidic residue may be cracked by heating the acidic residue, for example to a temperature of about 300°C (the exact temperature will depend upon specific hydrocarbons involved). Heating may drive off the more volatile fractions in the used lubricating oil. A gaseous fluid may be passed through the heated acidic residue during cracking. The gaseous fluid may comprise a hydrocarbon gas, for example, butane. The cracking of hydrocarbons in the acidic residue may continue until about 90% of available hydrocarbons have cracked into smaller fractions which are driven off from the remaining residue.

[0010] Concentration of the non-organic elements may continue until the non-organic elements are embedded in a solid matrix comprising carbon. The solid matrix may comprise a carbon-based polymer. The solid matrix may also comprise graphite. Such graphite may be produced if the acidic residue is heated by a direct flame. The solid matrix may have a large surface area to weight ratio and may be porous.

[0011] In accordance with a second aspect of the present invention, there is provided a catalyst for catalytic cracking of hydrocarbons, comprising a used lubricating oil residue comprising non-organic elements embedded in a solid matrix comprising carbon. The non-organic elements may be evenly distributed throughout the solid matrix, and may comprise at least a plurality of elements selected from the group consisting of: magnesium, aluminium, silicon, phosphorus, sulphur, chlorine, potassium, calcium, titanium, iron, copper, zinc, molybdenum, tin and lead. The solid matrix may be porous and may comprise a carbon-based polymer and/or graphite. The catalyst may be acidic. The used lubricating oil residue may be acidic. The used lubricating oil residue may be present in an amount of about 10 to 30% by weight of the catalyst. (The exact amount depends upon the structure of the acidic residue).

[0012] In a combustion test in the presence of oxygen, about 70% of the weight of the catalyst would be lost to combustion gases.

[0013] In accordance with a third aspect of the present invention, there is provided a method of cracking long-chain hydrocarbons, comprising: providing a catalyst in accordance with the second aspect of the present invention; and heating long-chain hydrocarbons in the presence of the catalyst and hydrogen or a hydrocarbon gas. The hydrocarbon gas may consist of a single type of gas or may include a mixture of two or more types of gases, and may be selected from the group consisting of methane, ethane, propane and butane. The long-chain hydrocarbons may be heated to a temperature of about 320°C. (The exact temperature will depend upon the composition of the long chain hydrocarbons).

[0014] The method may further comprise controlling the long-chain hydrocarbon dwell time in the presence of the catalyst. Limiting the dwell time may prevent the production of very short-chain hydrocarbons. The control step may comprise establishing a flow of hydrocarbon gas past the catalyst. Once past the catalyst, long-chain hydrocarbon cracking stops and thus the flow may be used to control the degree of cracking which occurs. The flow may be sufficient to flush cracked hydrocarbons beyond the catalyst.

[0015] The method may further comprise controlling the pressure of the long-chain hydrocarbons and the hydrocarbon gas in the presence of the catalyst. Increasing the pressure may bring about a need to increase the temperature of the long chain hydrocarbons.

[0016] Heavy or long-chain hydrocarbons in fuel oil include complex chain forms and structures with various functional groups, such as esters, acids, aromatics and polymers. Therefore, the non-organic elements in the catalyst of the present invention play an important role in cracking the specific compounds in fuel oil and hence the cracking phenomenon occurs conveniently at temperatures as low as 320°C. At the same time, manufacturing the catalyst from used lubricating oil is economically feasible.

[0017] Any type of heavy hydrocarbon may be cracked using the catalyst in accordance with the present invention in combination with heat and hydrocarbon gas. By changing the process temperature, pressure and/or gas flow, variations in the ratio of cracked hydrocarbons to raw material may be achieved. For example, by decreasing pressure (gases), the cracking rate increases, at constant temperature. Also, by increasing gas flow beyond a threshold level, long-chain hydrocarbons (not necessarily cracked) may be removed from the catalyst. Furthermore, by increasing the pressure when the gas flow is low, cracked hydrocarbon chains may join linearly to each other (polymerization).

[0018] The passage of ultra heavy hydrocarbons such as bitumen past the catalyst may yield a product with improved properties. For example, the resulting bitumen may be more resistant to ultra violet radiation and less prone to embrittlement or crazing during service life. In one experiment, the resistance of processed bitumen against heat and oxygen was measured and no losses on heating were observed up to 300°C for 10 hours.

[0019] Embodiments of the invention will now be described by way of example, with reference to the accompanying drawings, in which:-

[0020] Figure 1 shows schematically apparatus for catalytically cracking hydrocarbons in accordance with an embodiment of the present invention.

Preparation of Catalyst Embodying Present Invention

[0021] A quantity of used lubricating oil from an engine was chemically refined using a sulphuric acid treatment to yield an acidic residue or sludge. The acid residue contains the blend of non-organic elements or alloys which were acquired by the lubricating oil when used to lubricate the surfaces of various parts in the engine. The acidic residue is perhaps 20-25% by weight of the quantity of used lubricating oil. The acidic residue is heated by direct flame to about 300°C and butane gas is blown through it until about 90% of the residue has been cracked into smaller chain hydrocarbons and driven off. At the end, there remains a solid, acidic porous graphite and carbon-based residue (polymer), which has a large surface area to weight ratio, for use as a catalyst.

[0022] The composition of the catalyst, as determined by X-ray analysis, is set out in Table 1 annexed hereto, with the balance being graphite. The levels of the various non-organic elements listed in the table may vary between difference sources of used lubricating oil, without departing from the present invention. There is a general tolerance to the percentages in Table 1 which produce a viable catalyst.

Use of the Catalyst

[0023] Figure 1 shows schematically apparatus for catalytically cracking fuel oil according to an embodiment of the present invention. Many of the components of the apparatus will be familiar to those skilled in the art and thus a simple list of the components and reference numerals are provided in Appendix 1 attached hereto; only the key features will be described in detail.

[0024] Fuel oil at 320°C is supplied to a reactor (17) in which the catalyst is held. A hydrocarbon gas (such as methane) is additionally supplied to the reactor (17) in an amount greater than that which will be consumed during cracking of the fuel oil. Cracked products and surplus hydrocarbon gas exit from the top of the reactor (17) and pass to a distillation tower and separator (18). Surplus hydrocarbon gas is recycled and returned to the reactor (17). Distillate from the distillation tower (18) is collected and found to comprise mostly gasoline, kerosene and gas oil. (Chemical analysis of the distillate is set out in Appendix 2 attached hereto).

[0025] Variations in the pressure in the reactor (17) and the hydrocarbon gas flow rate will affect the type and quantity of product yielded. Changing the pressure will also cause a variation in the temperature. A pressure of approximately 1 atmosphere is required to crack at 320°C.

[0026] In a second trial, used lubricating oil was used in place of fuel oil, and similar results were obtained.

[0027] In a third trial, bitumen was used in place of fuel oil and pressure in the reactor was increased. This leads to a polymerization reaction, and production of a new bitumen with enhanced properties including improved resistance to ultra violet light.

[0028] In accordance with the present invention, the following may be achieved:

1. Using the new catalyst, one can readily crack the long chain hydrocarbons at elevated temperatures.
2. The hydrocarbon gases (any formula and chain length) control the cracking process. Varying gas flow rate may affect the cracking temperature. One can control the size of the hydrocarbon chain by varying gas flow rate and reactor pressure.
3. The cracked chains produced in this method are saturated and linear.
4. The amount of ultra short chain gaseous hydrocarbons produced during cracking are very small, while conventional processes produce a higher ratio of gas to naphtha.
5. To saturate the products, hydrogen gas is not necessary, although it could be used.
6. Bitumen with better properties and higher resistance against oxygen, heat and UV-radiation may be produced. This bitumen is less prone to crazing during service.
7. During catalytic cracking of fuel oil, about 8 wt% of the total raw material is converted to a heavy material called "residue", whilst the remainder cracks down to lighter products. Such residue from the reactor has enough sulphur and carbon as well as metals to be a suitable substitute for fillers in rubber, or for adding to bitumen.
8. The residue from the fuel oil, bitumen, and lube oil and oxidised bitumen, and acidic sludge (produced from the chemical refining of used lube oil) may be used as catalyst in producing a new fuel with octane number enhanced by alcohol.
9. Using this process, one can produce an improved bitumen material for use as an insulator for gas or oil tubes, roofs, building base, and metallic structures, and etc. The reforming of the molecular structure of bitumen (when polymerised) causes a change in properties so that it is suitable for these applications due to improved resistance to ultra violet light, greater ductibility and improved resistance to oxidation.

TABLE 1:

ANALYSIS OF NON-ORGANIC ELEMENTS IN CATALYST MADE FROM USED LUBRICATING OIL		
NAME	ELEMENT	PERCENTAGE
Magnesium	Mg	0.26
Aluminium	Al	0.044
Silicon	Si	0.125
Phosphorus	P	0.76
Sulphur	S	3.99
Chlorine	Cl	0.0014
Potassium	K	0.018
Calcium	Ca	1.56
Titanium	Ti	0.0023
Iron	Fe	0.28
Copper	Cu	0.018
Zinc	Zn	1.16
Molybdenum	Mo	0.0013
Tin	Sn	0.002
Lead	Pb	0.23

APPENDIX 1: REFERENCE NUMERALS AND COMPONENTS ILLUSTRATED IN FIGURE 1.

1. Heater
2. Burner
3. Stack
4. Orifice and differential pressure
5. Drain tank
6. Drain pump
7. Feed pump
8. Separator
9. Collector
10. Feed
11. By-pass valve
12. Expansion tank
13. Blocking vessel
14. Over flow line
15. Expansion line
16. Drain line
17. Reactor
18. Distillation Tower
19. Petrol pump
20. Light gas oil pump
21. Fuel tank
22. Heat exchanger
23. Fuel pump
24. Safety valve
25. Condenser
26. Reboiler

APPENDIX 2: CHEMICAL ANALYSIS OF DISTILLATE.

PHYSICAL AND CHEMICAL CHARACTERIZATION OF THE PRODUCTS OF CATALYTIC CRACKING OF FUEL OIL

PHYSICAL IDENTIFICATION :

The sample is light brown, homogeneous with low viscosity liquid, tt smells like hydrocarbon oil. The smell might be related to the aromatic compound in the sample.

ANALYSIS FROM BURNING :

It burns with a yellow flame followed by smoke and no ash remains. Therefore this sample should have aromatic compound, because it produces smoke. Of course unsaturated hydrocarbon burns with yellow flame and smoke, too. However, we noticed as reported , later, that the sample possess aromatic compounds rather than unsaturated hydrocarbon.

ACTIVE HYDROGEN TEST:

This sample does not react with sodium. Therefore it does not have any active hydrogen and neither any water.

SOLUBILITY :

Results of this test places the sample in group (I). This group consists of saturated holoalkane, arylehald, de aryle ether. And the solubility inactive aromatic ring is :

WATER	0%
NaOH	5%
HCl	5%

But it react either with cold or hot sulfuric acid.
(probably it sulphanets the aromatic ring).

TEST WITH PERMANGANATE :

This sample does not release sulfur and neither does change the violet color of permanganate when heated.

Distillation carried out in oil bath above 170°C and three parts were distilled as following:

1^{st} cut was a clear yellow liquid at 100- 130°C
2^{nd} cut was a yellow to brown liquid at 215-300°C
3^{rd} cut was a yellow wax after cooling.

ANALYSIS OF FUNCTIONAL GROUP :

Sample does not react with either chloroform or aluminum trichloride. The reaction mechanism is as following :

$$3\,ArH + CHCl_3 \longrightarrow Ar_3CH$$

$$Ar_3CH + R^+ \longrightarrow \underset{\text{color cation}}{Ar_3C} + 3HCl + RH$$

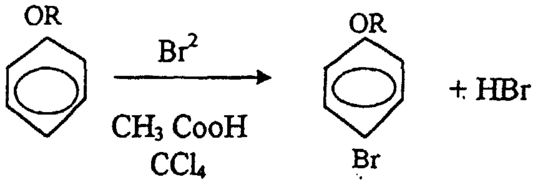
For any aromatic compound, triaryle.
Carbonium has identify color e.g. ;

Naphthalene	blue
Benzene	orange- red
Anthracene	green

Because $AlCl_3$ is a yellow compound, if any reaction takes place, it should change its color, but in the above case the color has not changed.

DE-ARYLE ETHER TEST :

This is a test with Br_2 in acetic acid or Br_2 in tetrachlorocarbon. This gives an additional reaction with aromatic ring.



All of the samples react vigorously with Br_2 in tetrachlorocarbon and release HBr, so that it changes the color of PH paper to red. Therefore, it proves that the HBr is produced All these samples before adding any Br_2 in tetrachlorocarbon are colorless, but as soon as adding Br_2 and CCl_4 becomes dark.

To find out the stoichiometry amount of Br_2 for 5 ml of the sample, titration carried -out with sample, but due to the dark color of titrant, the end point was not identified, however due to the reaction HBr gas constantly released.

This is an additional reaction for compounds such as phenol, aryle ether and all the aromatic ring with active groups.

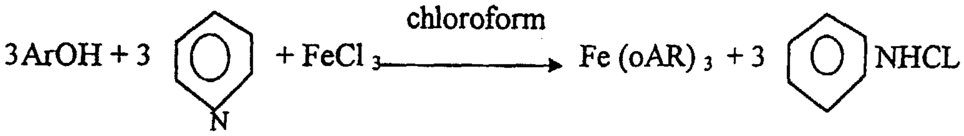
The color of the reaction is due to the dark ppt precipitate and is stable and can not separate them from solution by paper filter, but may partly be separated them by centrifugal force .

This test is also used for identification of double bond, of course in this case the reaction is substitution reaction and during this reaction some gases should release.

TEST FOR PHENOL

Bromine (Br_2) in glacial acetic acid reacts with phenol and a colorful solution is resulted. Based on the phenol composition, the color of the solution is different such as green, red, purple, blue, ..., etc.

If there is any phenol in the solution, the following reaction may occur, however the solution color didn't change.



By adding $FeCl_3$ / $CHCl_3$ which is yellow to the sample, the system must turn in color, but no color change happened. Therefore there is no phenol in the system.

In conclusion, The sample contain Aryl Ether and alkane and maybe alkane, but the IR shows that most of the sample is alkane.

SOME USEFUL OBSERVATIONS:

Activated carbon was used to decolorize the sample. However, after mixing the solution with activated carbon for ten minutes, the yellow color of the solution did not change. Therefore, the color of the sample is not due to the impurities and it is due to the nature of the compounds in the solution.

For identification of the distillates a GC test run was performed with the first cut of the solution (Fig 6). The GC spectra shows that the solution is mostly saturated hydrocarbon chain rather than the long chain.

Of course the separation can be done by a suitable chromatography column. The column should be polar.

FT-IR SPECTRA :

The 2nd and 3rd part of distillation IR peaks show saturated hydrocarbon with straight chain.

At 3000 Cm $^{-1}$ shows C-H aliphatic also at 1460 and 1377 Cm $^{-1}$ a sharp peak shows CH_2 and CH_3 (Fig4 and 5) the only difference in these two IR spectra is a week peak at left hand side of 3000 Cm $^{-1}$ (in Fig 4) and also a weak peak at 1630 Cm $^{-1}$ shows alkene and aromatic that are very weak in the sample.

CONCLUSION :

Fuel oil has a long hydrocarbon chain, ester, acids, aromatic with long chain and polymer. According to the performed tests we can could conclude that the fuel oil is broken down to a sample with shorter hydrocarbon chain and with small amount of active aromatic ring.

Claims

1. A method of producing a catalyst for cracking hydrocarbons, comprising:

   providing a used lubricating oil comprising traces of non-organic elements; and
   concentrating the non-organic elements.

2. A method according to claim 1, wherein the non-organic elements are concentrated by chemically refining the used lubricating oil to produce an acidic residue, and cracking hydrocarbons in the acidic residue.

3. A method according to claim 2, wherein the used lubricating oil is chemically refined by treating with a strong acid, for example sulphuric acid.

4. A method according to claim 2 or claim 3, wherein cracking hydrocarbons in the acidic residue comprises heating the acidic residue.

5. A method according to claim 4, wherein the acidic residue is heated to about 300°C.

6. A method according to claim 4 of 5, wherein cracking hydrocarbons in the acidic residue further comprises passing a gaseous fluid through the heated acidic residue.

7. A method according to claim 6, wherein the gaseous fluid comprises a hydrocarbon gas, for example butane.

8. A method according to any one of claims 1 to 7, wherein the non-organic elements are concentrated by a factor of about 4 by chemical refining.

9. A catalyst for catalytic cracking of hydrocarbons, comprising a used lubricating oil residue comprising non-organic elements embedded in a solid matrix comprising carbon.

10. A catalyst according to claim 9, in which the used lubricating oil residue is acidic.

11. A catalyst according to claim 10 in which the acidic used lubricating oil residue is present in an amount of about 10 to 30% by weight of the catalyst.

12. A catalyst according to any one of claims 9 to 11 in which the solid matrix comprises a carbon-based polymer and/or graphite.

13. A method of cracking long-chain hydrocarbons comprising:

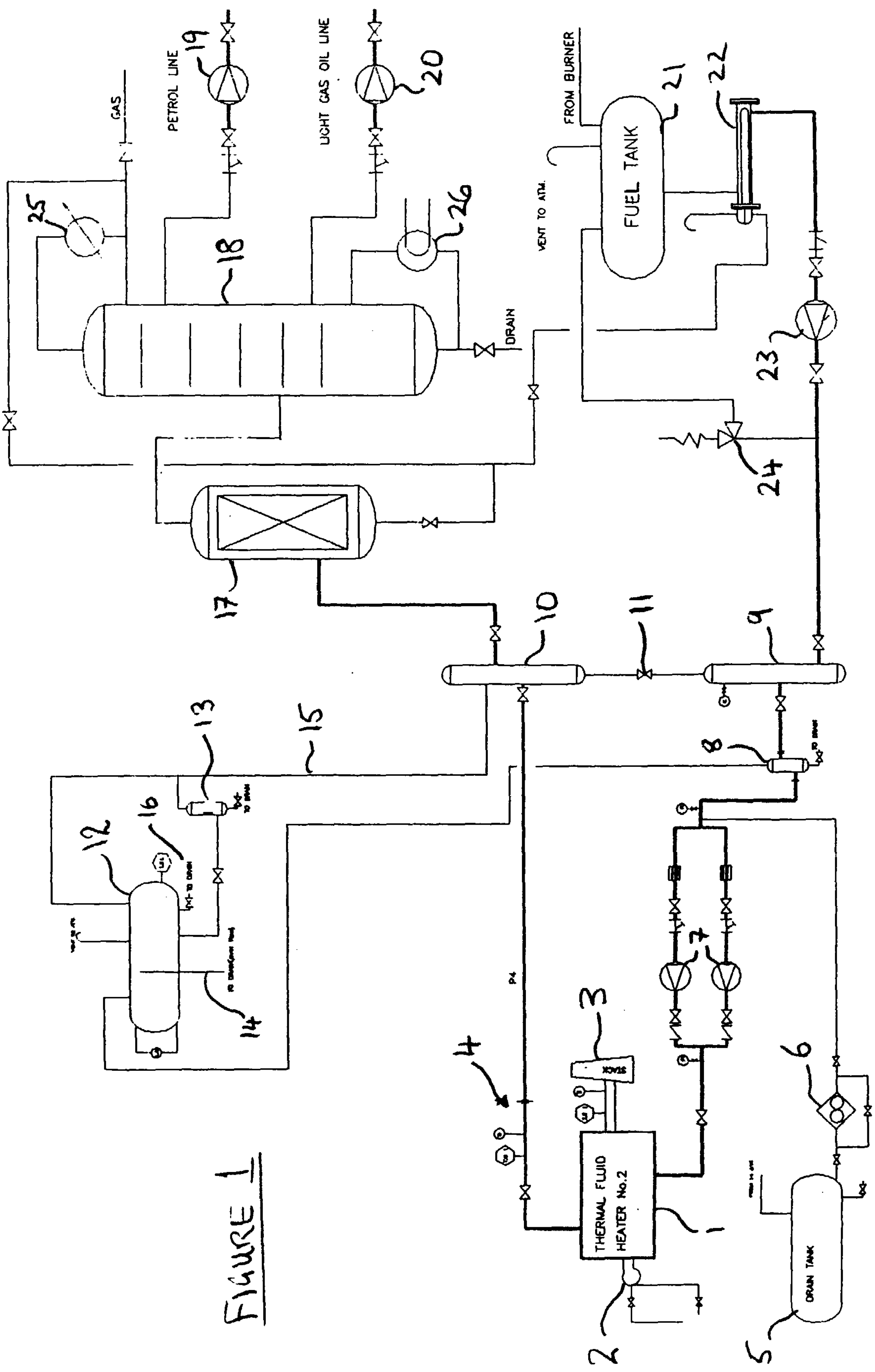
providing a catalyst manufactured in accordance with any one of claims 1 to 8 or according to any one of claims 9 to 12; and
heating long-chain hydrocarbons in the presence of the catalyst and hydrogen gas or a hydrocarbon gas.

14. A method according to claim 13, in which the hydrocarbon gas is selected from the group consisting of methane, ethane, propane and butane.

15. A method according to claim 13 or 14, further comprising controlling the long-chain hydrocarbon dwell time in the presence of the catalyst, for example by establishing a flow of hydrocarbon gas past the catalyst.

16. A method according to any one of claims 13 to 15, further comprising controlling the pressure of the long-chain hydrocarbons and the hydrocarbon gas in the presence of the catalyst.

17. A method according to any one of claims 13 to 16, in which the long-chain hydrocarbons are provided as bitumen, with conditions (e.g. temperature, flow rates and/or pressure) being such that cracked bitumen hydrocarbons polymerize whilst in the presence of the catalyst.


THERMAL FLUID HEATER No.2
STACK
DRAIN TANK
FUEL TANK
FROM BURNER
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PETROL LINE
LIGHT GAS OIL LINE
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FIGURE 1